free host. Only when Li^+ or Na^+ were present did additional signals appear at δ 2.508, 3.049, and 7.355 (Li^+ complex, **7**), and at 2.485, 2.974, and 7.320 (Na^+ complex, **11**). The peak intensities of complexed and uncomplexed **1** indicated that, within experimental error, all guest present was complexed.

When violently shaken (quartz tubes) with 1 mL of 0.0028 M solutions of **1** in $CDCl_3$ at 30 °C, a 6 M solution (1 mL) of LiBr converted **1** into **8** in ~8 h and a 6 M solution (1 mL) of NaBr converted **1** into **10** in <1 h (^1H NMR). A similar extraction with 1 mL of 0.0028 M solution of **1** in $CDCl_3$ of 1 mL of water that was 0.1 M in both NaCl and LiCl gave, after 284 h, 0% **1**, 89% **8**, and 11% **6** (^1H NMR). Thus **1** in $CDCl_3$ extracts NaCl from water ca. eight times as fast as LiCl. Extraction experiments with separate NaCl and LiCl solutions provided the same rate factor. Similar extractions with **1** in $CDCl_3$ of 1.5 mL of aqueous solutions of 4.5 M KBr, 2 mL of 3 M $MgBr_2$, 1 mL of 6 M $CaBr_2$, and 2 mL of 3 M $SrBr_2$ for from 24 to 180 h gave no evidence of any ions being complexed except for traces of Na^+ and sometimes Li^+. In all cases, the trace amounts were slowly scavenged from the bulk amounts of the other ions (^1H NMR and mass spectra).

These experiments provide the following conclusions. (1) A powerful ligand system of D_{3d} symmetry has been composed solely of *p*-methylanisole units, which when taken singly are poor ligands for metal ions.[15] (2) This spherand strongly complexes Li^+ and Na^+, since these ions can fill the enforced cavity and thus eliminate the electron-electron repulsions designed into the free ligand system. (3) Complexation rates of these ions in $CDCl_3$ at 30 °C are on the human time scale, but the decomplexation rate of Na^+ and Li^+ at 30 °C must be extremely slow. (4) Spherand **1** in $CDCl_3$ extracts NaBr from water eight times fater than LiBr, the scavenges from concentrated solutions of KBr, $MgBr_2$, $CaBr_2$, and $SrBr_2$ trace amounts of Na^+ and Li^+ without complexing the bulk ions. (5) Since Li^+ and Mg^{2+} on the one hand, and Na^+ and Ca^{2+} on the other, possess similar diameters, the high selectivity seems associated with both diameter and charge. Probably the selection of Li^+ and Na^+ over Mg^{2+} and Ca^{2+} is kinetic. The selection of Li^+ and Na^+ over that of the larger ions may either be kinetic or thermodynamic or both.

Molecular model examinations of **1** and of spheres of diameter 1.5-1.9 Å (e.g., Li^+ and Na^+) indicate that, to complex or decomplex, the cations must pass through a lipophilic sleeve composed of three CH_3-O groups. At the halfway point, the cations can have only one to two ligands external to the spherand and none in the spherand. This structural feature explains why complexation-decomplexation activation energies for these spherand-metallospherium salts are so high, particularly for the divalent ions.

We are designing, synthesizing, and studying the differential binding properties of spherands and hemispherands[16] composed of methoxycyclohexane, cyclic urea, pyridine oxide, cyclic ketone, and lactam units whose geometries resemble portions of **1**. Both atoms and ions as guests are being studied.

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(7) This family name is composed from the word "sphere" (derived from the Greek sphaira and Latin sphaera) and from the suffix "and" taken from the word "ligand". The suffix "ium" for the complexes is appropriate since cation names have this ending, just as anion names have endings such as "ide" or "ate". The inserting of the letters "spher" into the names of the metal salts parallels the chemical operation of inserting a spherical ligand shell of oxygens between the cation and the anion. Thus complexed lithium chloride becomes a lithiospherium chloride (e.g., **6**) and a complexed sodium perchlorate becomes a sodiospherium perchlorate (e.g., **11**).

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(9) If the dihedral angles between the benzene rings in CPK models of **1** are opened to ~70-80° and the Ar-Ar bond angles all deform by 10-20 Å, the two methyl groups (one on each side) can be turned inward to give a highly compressed conformation without a central cavity. We believe such conformations to be highly unlikely. The barrier to rotation around the Ar-OCH_3 bond appears in models to be high. Both X-ray crystallography and the temperature-dependent ^1H NMR spectrum of **1** and its complexes are being examined to check these predictions.

(10) Estimates of hole diameters are made by inserting graded spheres (ball bearings) into CPK models of **1**.

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(12) Carbon and hydrogen analyses were within 0.30% of theory, and ^1H NMR and mass spectra were consistent with the structural assignments.

(13) Many other oxidants were tried but most of them failed. The reaction has been applied to making aryl-aryl bonds in a variety of systems.

(14) The mass spectra of the metallospherium salts gave base peak *m/e* values corresponding to the metal salts of the corresponding phenols, in which one methyl has been lost with complexes of Li^+ and Na^+.

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(16) The cyclic host composed of three bonded *p*-methylanisole units bridged by a $CH_2(OCH_2CH_2)_2OCH_2$ chain (compound **37** of ref 15) might be called a hemispherand, since half of the molecule has an enforced arrangement of the electrons of the three anisole oxygens and consequently exceeds the crowns in binding power of Na^+, K^+, Rb^+, and Cs^+ ions in $CDCl_3$. The X-ray structure of this free host shows the three methoxyl groups oriented as in structure **1**, but the crown part contains one to two inward-turning CH_2 groups (one disordered) which tend to fill the potential cavity. The OCH_2CH_2O oxygens are distant, and the OArArO oxygens are close to one another (private communication from I. Goldberg). This structure illustrates in the same molecule how three crown or cryptand units organize to fill potential holes, whereas three spherand units are unable to do so.

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An Unusually Long Cobalt-Carbon Bond. Molecular Structure of *trans*-Bis(dimethylglyoximato)(isopropyl)(pyridine)cobalt(III). Implications with Regard to the Conformational Trigger Mechanism of Cobalt-Carbon Bond Cleavage in Coenzyme B_{12}

Sir:

Homolytic cleavage of the Co-C bond is generally accepted as a key step in the mechanism of action of many enzymes which require a B_{12} coenzyme.[1-3] The factors which promote this cleavage are not yet understood.[1,3] Recent work with dioldehydrase by Abeles and his co-workers[1] has demonstrated that modification of the side chains on the periphery of the corrin ring leads to considerable variation in coenzyme activity. Since the changes in the side chains were not such as to alter significantly the electronic properties of the corrin ring system, it is unlikely that the variation in activity resulted from inductive effects. Variations in the ease of formation of cob(II)alamin correlated, to some degree, with alterations in activity.[1] A reasonable hypothesis advanced to explain these and other results is that specific tight interactions between the enzyme and coenzyme bring about distortion of the corrin ring system, thus facilitating cleavage of the Co-C bond. Comparisons between the stability of model organocobalt compounds and organocobalamins has led Halpern[3] to suggest that steric effects of the corrin ring may be important in promoting dealkylation.[16]

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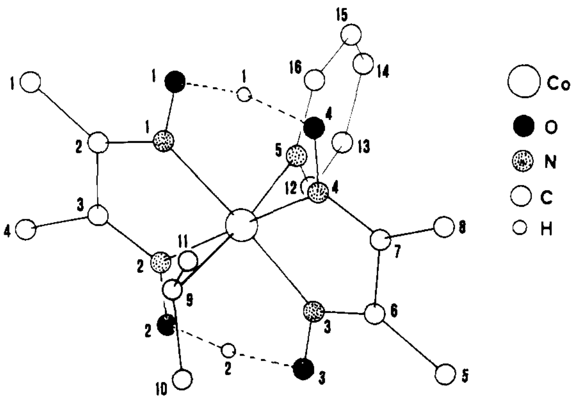

Figure 1.

The title complex, prepared by standard procedures,[2,3] crystallizes from acetone-water in the monoclinic space group $P2_1/c$ with a = 8.314 (3), b = 28.930 (7), c = 9.019 (3) Å; β = 117.52 (3)° (Mo $K\alpha$); and Z = 4 formula units $CoO_4N_5C_{16}H_{26}$; observed and calculated densities are 1.41 and 1.42 g cm^{-3}, respectively. Three-dimensional X-ray diffraction data were collected on an automated SIEMENS-AED diffractometer using the Mo $K\alpha$ radiation and the θ-2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by the least-squares method with anisotropic temperature factors for nonhydrogen atoms to a present conventional R value of 0.033 including hydrogen atom contributions. A total of 3214 independent reflections, having $\theta_{max} \leq 28°$ and $I > 3\sigma(I)$ was used in the final calculations. No absorption correction was applied ($0.15 \leq \mu R \leq 0.25$).

The crystals consist of discrete $(py)Co(DH)_2(i\text{-}C_3H_7)$ units (Figure 1). The essentially planar (±0.005 Å) axial py ligand is nearly perpendicular (86.5°) to the equatorial $(DH)_2$ coordination plane and bisects the angles N(1)-Co-N(4) and N(2)-Co-N(3).

The geometry of the $(py)Co(i\text{-}C_3H_7)$ fragment is characterized by exceptionally long Co-C and Co-N bond lengths which are 2.085 (3) and 2.099 (2) Å, respectively, with a C-Co-N angle of 175.4 (1)°. Thus C(9) and N(5) are pushed away from N(3) and N(4), whereas the C(10) and C(11) atoms are above this side of the equatorial ligands, nearly along the Co-N(3) and Co-N(4) directions, Furthermore, the C-Me bond lengths are both 1.507 (4) Å with a Me-C-Me angle of 112.3 (3)°, whereas the Co-C-Me bond angles are 114.3 (2) and 114.0 (2)°. A comparison with the corresponding bond lengths and angles in propane[4] and isobutane[5] reveals a significant decrease (0.02 to 0.03 Å) of the C-Me bond length which parallels a flattening of the tetrahedron around the central carbon atom in the plane of Co and Me groups, as shown by the sum (340.6°) of the angles around C(9) and involving these substituents. These parameters suggest that hybridization of C(9) is modified upon coordination.

In contrast to such distortions, the $Co(DH)_2$ unit appears to be relatively unaffected by steric strain with normal bond lengths and angles[6] and the molecular parameters found here are roughly similar to those for $(py)Co(DH)_2CH_3$.[6] The plane of the N(1), N(2), C(1), and C(4) atoms (coplanar within ±0.003 Å) is parallel to the plane of the N donors (coplanar within ±0.002 Å), their angle being 0.2°. The plane of the N(3), N(4), C(5), and C(8) atoms makes angles of 4.3 and 4.2°, respectively, with the above planes, bending toward the $i\text{-}C_3H_7$ group. The Co atom is displaced 0.022 Å from the N-donor plane toward the py ligand.

The above distortions found in the $Co(DH)_2$ unit are very small if compared with those found in $R_3PCo(DH)_2X$ (R = $c\text{-}C_6H_{11}$, C_6H_5, C_4H_9; X = Cl, CH_3), where the interplanar angle between the two DH units ranges from 6 to 16° and the displacement of cobalt above the N-donor atoms, from 0.04 to 0.11 Å.[7] The distortions caused by very large bulky ligands result from steric interactions of these ligands with the peripheral methyl groups. For more bulky alkyl ligands, the metal-to-donor atom bond apparently lengthens without inducing steric distortions in the equatorial ligand system.

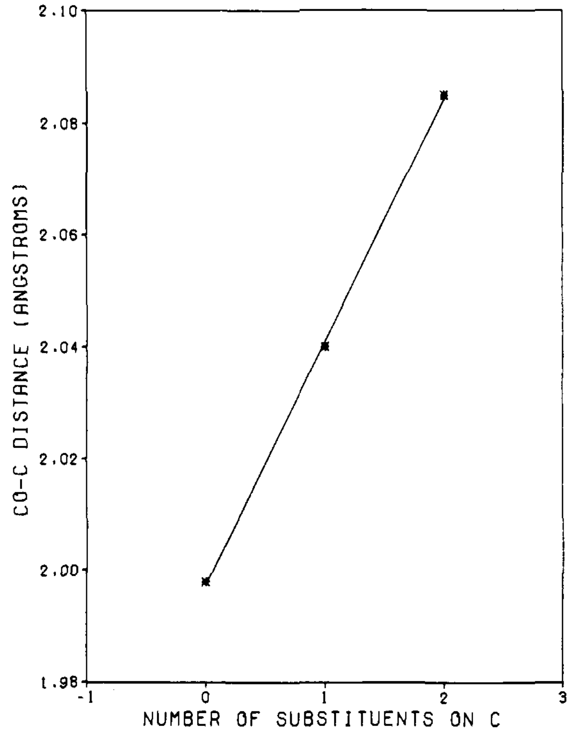

Figure 2. Plot of Co-C bond length vs. the number of substituents on the alkyl carbon bonded to the cobalt for $pyCo(DH)_2R$. Points from left to right are CH_3,[6] CH_2COOCH_3,[8] and $i\text{-}C_3H_7$.

The long Co-C bond is the most interesting aspect of this structure. For $pyCo(DH)_2R$, there is a clear linear relationship between the Co-C bond length and the number of substituents on the methyl group (Figure 2). Although a good linear relationship (correlation coefficient = 0.9998) of this type has not been noted previously, examination of literature data reveals that the trend is general, if one allows for differences in the trans ligand[8-12] (see ref 13 for a summary). In particular, the Co-C bond length in adenosyl B_{12} is 2.05 Å,[12] consistent with the value expected for a monosubstituted methyl group, although it must be borne in mind that a corrin ring is present in B_{12}. The Co-N bond lengths in the py complexes follow the order $CH_2CO_2CH_3 < CH_3 < i\text{-}C_3H_7$ (2.040 (3), 2.068 (3), and 2.099 (2) Å, respectively), and undoubtedly this trend reflects both steric and inductive effects.[13]

In Figure 3, we compare the ^{13}C NMR shift of coordinated $P(OCH_3)_3$ as a function of σ^* of various alkyl substituents[14] in $P(OCH_3)_3Co(DH)_2R$. We have shown that this NMR parameter is a good measure of the inductive effect of the ligand trans to $P(OCH_3)_3$.[15] Of the alkyl ligands examined, ethyl has the maximum inductive effect. Bulkier ligands, even those with more negative σ^* values, have, at best, inductive effects comparable with that of ethyl. This finding almost certainly reflects long Co-C bonds, as we have shown for $i\text{-}C_3H_7$, and appears to be general. From molecular models, it is clear that the adenosyl moiety will also be subject to such effects, in keeping with the suggested steric trigger mechanism[1-3] of Co-C bond cleavage in coenzyme B_{12} reactions.

It is conceivable that in the enzyme-coenzyme complex a distortion of the corrin ring could be induced partly or wholly by displacement of the axial benzimidazole ligand toward a shorter Co-N bond. We are presently engaged in attempts to

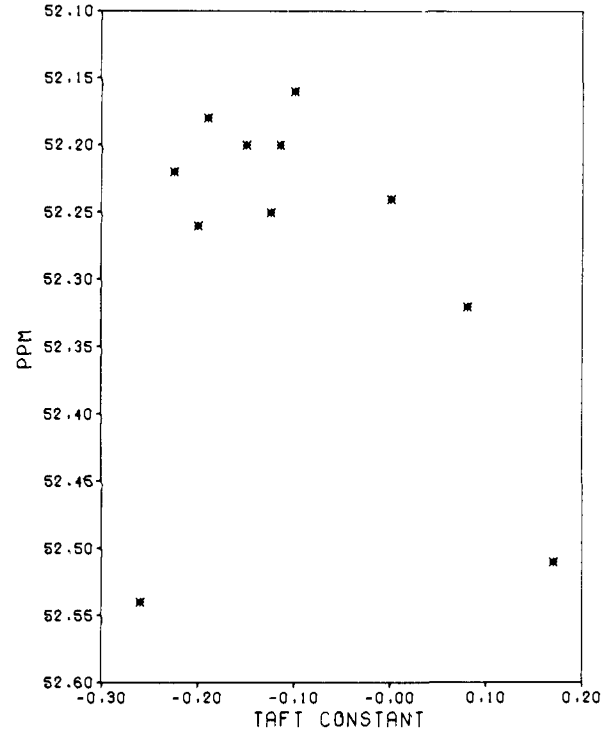

Figure 3. Carbon-13 shift of coordinated trimethyl phosphite in $(CH_3O)_3PCo(DH)_2R$. Points from left to right are $CH_2Si(CH_3)_3$, 3-C_5H_{11}, c-C_5H_9, *i*-C_3H_7, c-C_6H_{11}, *i*-C_4H_9, C_2H_5, CH_3, $(CH_2)_2C_6H_5$, and $(CH_2)_3CN$.

synthesize, crystallize, and structurally characterize complexes of the type $LCo(DH)_2(i\text{-}C_3H_7)$, in which L is a very bulky ligand. If such ligands distort the $Co(DH)_2$ moiety, the Co–C bond length in such compounds could be even longer than that found here.

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Supplementary Material Available: A listing of structure factors, atomic parameters, hydrogen atom coordinates, and bond lengths and angles of $Me_2CHCo(DH)_2py$ (12 pages). Ordering information is given on any current masthead page.

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(16) NOTE ADDED IN PROOF. A recent paper discusses steric factors influencing Co–C bond cleavage in cobalamins (Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601). However, it was suggested that the corrin ring system buckles to accommodate bulky alkyl substituents on Co and this distortion leads to cleavage of the Co–C bond.

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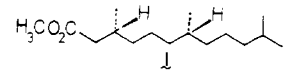
A Stereocontrolled Approach to Acyclic Systems. Stereorelay in Charge-Directed Alkylations via Organopalladium Templates

Sir:

One of the most exciting challenges in synthetic methodology is control of stereochemistry in conformationally nonrigid systems. We report herein a new approach based upon the utilization of a transition metal complex as a temporary template to relay stereochemical information in a normally conformationally nonrigid system.[1] This concept has been examined within the context of the synthesis of an acyclic unit **1** that constitutes the side chain for α-tocopherol (**2**) or vitamin K (**3**).[2a-d] During the course of this investigation, an approach for defining the relative stereochemistry of such remote centers as in **1** emerged.[3]



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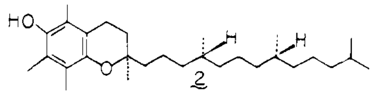

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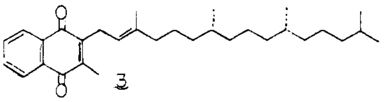

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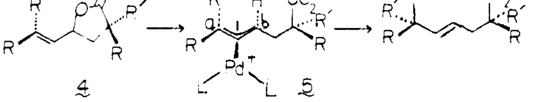
In this approach, ring stereochemistry is relayed along a π system by a palladium complex[4] as shown in eq 1. For such an approach to be successful, (1) ionization of the vinyl lactone **4** must occur from one conformation, (2) the intermediate π-allylpalladium complex **5** must retain its stereochemistry, and (3) the nucleophile must attack regioselectively at the carbon of the allyl system distal to the carboxylate (i.e., site "a" in **5**).



(1)

To check the ability of the charge to direct the approach of the nucleophile, the lactone **6a**[5,6] was reacted with methyl sodiomalonate and 3 mol % tetrakis(triphenylphosphine)palladium in refluxing THF to give after initial workup a >90% yield of product shown to be **7a**[6] (δ 5.52 (ddd, *J* = 15, 7, 7 Hz), 1 H, 5.43 (dd, *J* = 15, 8 Hz, 1 H), 1.05 (d, *J* = 7 Hz, 3 H), decoupling at 2.34 collapses signal at 5.52 (br d, *J* = 15 Hz)) with >98% regiospecificity. The exclusive formation of the *E*

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